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Research Conducted in the last year has focussed on the prparation and cleaning of ZnO substrates and on the initial growth of InAlN by Metal Organic Molecular Beam Epitaxy (MOMBE). Significant improvement in surface morphology of the substrates has been verified by Atomic Force Microscopy (AFM). High resolution X-ray diffraction (HRXRD) has shown an improvement in the substrate quality as indicated by a very small full-width half-maximum (FWHM) for the ZnO peak. Annealing studies of the ZnO substrates revealed that no substantial loss of oxygen from the ZnO suface could be detected by Auger electron spectroscopy, nor could a change in surface morphology be found by AFM. Several InAlN samples have been grown on the ZnO substrates and have been analyzed by electron microprobe and powder X-ray diffraction to determine the ternary compositions. Thus far the nitride compositions are approaching the lattice matched composition of $In_{.325}Al_{0.675}N$ and significant improvements in Surface morphology have been acheived by varying traditional growth parameters.

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Growth of Lattice Matched InAlN on ZnO by MOMBE

Introduction

Research conducted in the last year has focused on the preparation and cleaning of ZnO substrates and on the initial growth of InAlN by Metal Organic Molecular Beam Epitaxy (MOMBE). Significant improvement in surface morphology of the substrates has been verified by Atomic Force Microscopy (AFM). High resolution X-ray diffraction (HRXRD) has shown an improvement in the substrate quality as indicated by a very small full-width half-maximum (FWHM) for the ZnO peak. Annealing studies of the ZnO substrates revealed that no substantial loss of oxygen from the ZnO surface could be detected by Auger electron spectroscopy, nor could a change in surface morphology be found by AFM. Several InAlN samples have been grown on the ZnO substrates and have been analyzed by electron microprobe and powder X-ray diffraction to determine the ternary compositions. Thus far the nitride compositions are approaching the lattice matched composition of $In_{0.325}Al_{0.675}N$ and significant improvements in surface morphology have been achieved by varying traditional growth parameters.

ZnO Surface Preparation

The preliminary work in this project was aimed at optimizing the ZnO substrate quality in order to reduce contamination and any other deleterious effects in subsequently deposited InAlN films. Supply and fabrication of the ZnO substrates was provided by an external source to the University of Florida and our experimental feedback was used to modifiy their existing proprietary ZnO production technology. Thus far, three sets of ZnO substrates have been supplied to us and labeled Old Stock Crystals (OSC), Set #1, and Perfection Standard. The AFM and X-ray results presented in this report show improvements in the surface morphology and substrate quality as a result of modifications in either ZnO handling, storage and/or fabrication. However, due to the proprietary status of this technology, the modifications were not reported to us.

A Digital Instruments Nanoscope III multimode AFM was used to image the surfaces of the ZnO substrates. Three different modes of operation are available for data collection (contact, non-contact and tapping mode) on the AFM. Tapping mode was chosen to image the substrates because it is less likely to damage the sample than in contact mode by the elimination of lateral forces (friction or drag) between the sample and tip. Additionally, in the tapping mode, the inherent water layer on the substrate surface is penetrated by the tip during the scans (tapping) allowing for the imaging of the underlying surface.

The first set of ZnO substrates (Set #1) received were very rough on the 10 to 20 nanometers scale, with multiple white and dark areas as shown in Fig.1. In the AFM micrographs, the white areas are raised above the surface, while the dark areas are sunk below the surface. Suspecting these raised areas to be debris from handling and storage, we used an acetone wipe followed by a methanol wipe to clean the surface. The reduction in the white areas was dramatic, as shown in Fig.2, with a surface a roughness of less than a nanometer.

The effects of heating the samples to 400°C or 500°C for 0.5 hours in N_2 are shown in the data in Fig.3. While these surfaces were not cleaned as before, the effects of excluding the debris on the surface data can be seen by using a selected area of the scan (box). Comparing the box data of ~~**0.31nm**~~ 0.353 to the cleaned surface data of **0.356 nm** we find very similar roughness values. Therefore we don't have any evidence that heat treatments under these conditions roughen the ZnO surface.

The representative data from the Perfection Standard ZnO set is shown in Fig.4. These surfaces were analyzed without cleaning and were still far less contaminated and smooth (RMS=0.24nm). All measures of the surface displacement and roughness indicate the higher quality of the Perfection Standard sample versus those received in Set #1

The X-ray diffraction data collected is summarized in Table 1 for the ZnO substrates from Set#1, Old Stock Crystals (OSC) and the Perfection Standard set. The data was collected from high resolution X-ray diffractometer ω scans with a 5 crystal configuration. Data was also collected with both ω and $\omega/2\theta$ scans with two additional crystals just before the X-ray detector to

improve resolution (7 crystal or triple axis mode). It should be noted that the inherent FWHM is lower in the triple axis mode and that the $\omega/2\theta$ scan is not very sensitive to defects. The sample from set #1 exhibited very broad (0002) peaks with FWHM's of 165 (see Fig.5) and 155 arc sec in the 5 crystal configuration. With better resolution in the 7 crystal configuration, the ω FWHM was 67 arc sec (Fig.6), while the $\omega/2\theta$ was only 12.8. The OSC sample had a more peaked (0002) diffraction peak and as a result the FWHM was only 70 arc sec in the 5 crystal configuration. However the diffraction peak had a very broad shoulder on the low angle side, similar to the peak structure of the samples in set #1. This peak was more symmetric with the 7 crystal system with FWHM's of about 15 arc sec. The FWHM's of the Perfection Standard set were very good in both the ω and the $\omega/2\theta$ scans. In general, the FWHM's were in the neighborhood of 10-16 arc sec (Fig.7), which is quite good.

Table 1.

Sample		FWHM of (0002) Peak (arc sec) ω scan	$\omega/2\theta$ scan
Set #1	(a)	165*	
	(b)	155*	
	(c)	67#	12.8
OSC	(a)	70*	
	(b)	14.8#	13.5
Perfection Standard	B	8.8#	14.5
	C	15.7#	14.0
	D	16.0#	14.4

*Data collected with 5 crystal configuration
#Data collected with 7 crystal configuration

One of the perfection standard wafers was analyzed by cross-sectional transmission electron microscopy. A bright field image (g_{220}) of the substrate is shown in Fig. 8. It is clear that the ZnO bulk has a very high dislocation density ($\approx 10^{10}/cm^2$).

Auger electron spectroscopy was used to measure the surface concentration of oxygen before and after heating the ZnO to 500°C for 0.5 hour. The ratio of O/Zn peak-to-peak height was 0.73 and 1 for as-received surfaces before and after heat treatment, respectively. Thus, there is no evidence of heat treatment reducing the surface oxygen. This interpretation is complicated by the fact that the as received, unheated surface was contaminated by carbon, and by the fact that all samples were exposed to air after heating. To attempt to remove the uncertainty of carbon contamination, the surfaces were sputtered for 30 seconds with argon ions (estimated depth of 10nm) and the samples reanalyzed. The O/Zn ratio for these samples were 0.76 and 0.82 for the unheated and heated samples, respectively. Our conclusion remains the same; these data do not substantiate loss of O from the ZnO surface during heating to 500°C.

Growth of InAlN

Metalorganic molecular beam epitaxy (MOMBE) has been used to grow $In_xAl_{1-x}N$ layers on ZnO. Initial experiments have focused on the calibration and characterization of the ternary compositions as a function of growth parameters. In addition, adjustments have been made to the conventional growth conditions in order to improve the $In_xAl_{1-x}N$ surface morphologies. The compositions of some of the recently grown films as determined by X-ray powder diffraction are shown in Table 2.

A series of growth runs has been conducted in order to calibrate the In mole fraction with precursor flow rates. The most recently grown compositions are approaching $In_{0.325}Al_{0.675}N$, which is the ternary lattice matched composition predicted by Vegard's law.

Table 2.

Sample ID	$In_xAl_{1-x}N$	Comments
50601-1	$In_{0.19}Al_{0.81}N$	
50609-1	$In_{0.28}Al_{0.72}N$	
50607-1	$In_{0.36}Al_{0.64}N$	
50613-1	$In_{0.37}Al_{0.63}N$	Morphology substantially improved with reduced ECR N_2 flux (nearly specular at 10KX SEM)

Determination of the ternary compositions of these early growth iterations has been conducted using X-ray powder diffraction and electron microprobe analysis on samples deposited on GaAs or Si. Two samples were also grown on ZnO, 50607-1 and 50613-1, and are currently under analysis to determine the degree of intermixing at the ZnO/AlInN interface by ion channeling, and to determine the defect structure by XTEM. The surface morphology of the nitride films was improved dramatically by reducing the nitrogen flow to the ECR plasma source. Further investigation of the cause of this improvement is in progress.

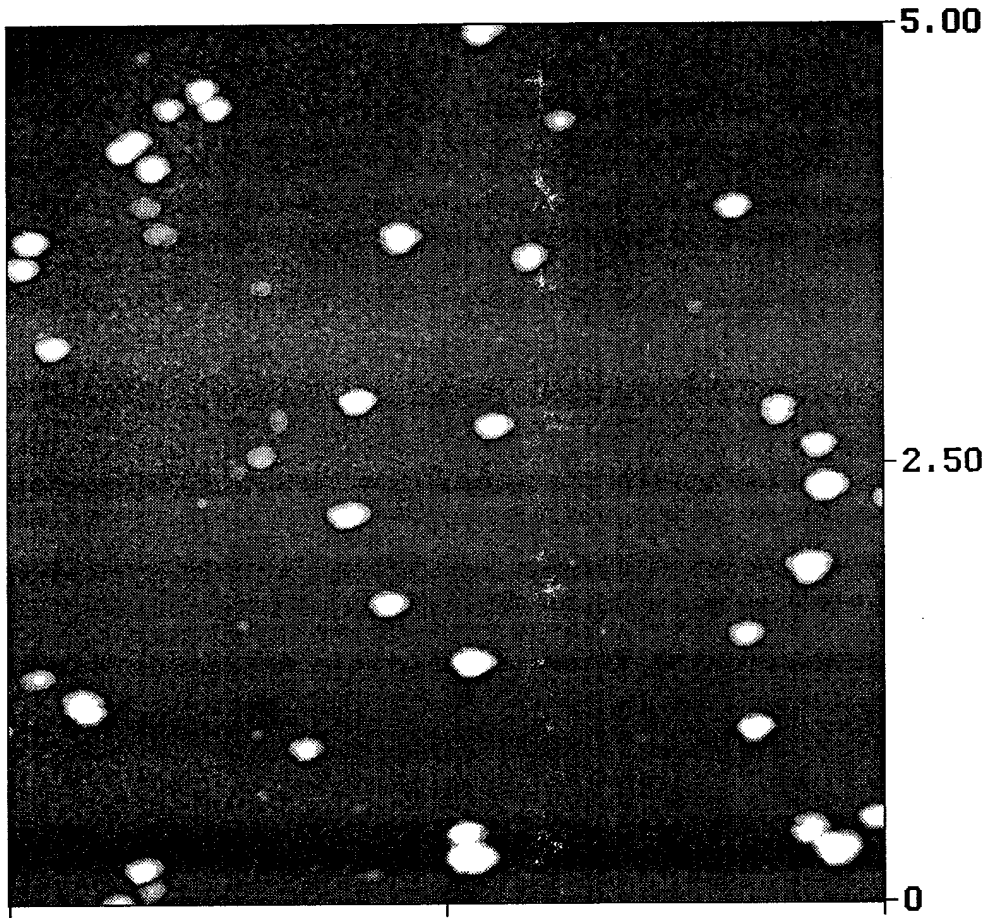
The compositional analysis techniques employed thus far are equally effective for films grown on different substrate materials, allowing for the use of Si or GaAs substrates and the conservation of the limited ZnO substrate pieces. However, the resolution of electron microprobe and x-ray powder diffraction is only sufficient to predict the composition and lattice mismatch within a few percent. Fine tuning the compositions to bring the lattice mismatch within 10^{-3} or better will require X-ray rocking curve analysis. The 5-crystal high resolution x-ray diffractometer available at the University of Florida is more than sufficient for this kind of analysis. However, the samples characterized with this technique should be epitaxially grown on ZnO. Further growth experiments will be limited by our supply of ZnO substrates.

Summary

ZnO substrates of epi-ready quality have been produced and are now in use for the deposition of $In_xAl_{1-x}N$ films grown by MOMBE. FWHM's of the substrate are at an acceptible level and ZnO substrate surface contamination has been minimized. ZnO has been found to remain stable up to temperatures of 500°C. Auger analysis could not detect any oxygen loss nor could AFM detect any change in substrate surface morphology. Finally, $In_xAl_{1-x}N$ films have been grown by MOMBE with compositions nearing that of lattice matched $In_{0.325}Al_{0.675}N$ and nitride film morphologies have been improved by using a reduced nitrogen flow to the plasma source.

Peak | Surface Area | Summit | Zero Crossing | Stopband | Execute | Clear

Roughness Analysis



ZnO Set#1 as received

Image Statistics

Z range	93.053 nm
Mean	-0.0009 nm
Rms (Rq)	7.411 nm
Mean roughness (Ra)	3.069 nm
Max height (Rmax)	93.053 nm
Surface area	25.459 µm²
Surface area diff	1.836 %

Box Statistics

Mean
Rms (Rq)
Mean roughness (Ra)
Box x dimension
Box y dimension

Peak off | Area on | Summit off | Zero Cross off

Fig. 1

Peak | Surface Area | Summit | Zero Crossing | Stopband | Execute | Clear

Roughness Analysis

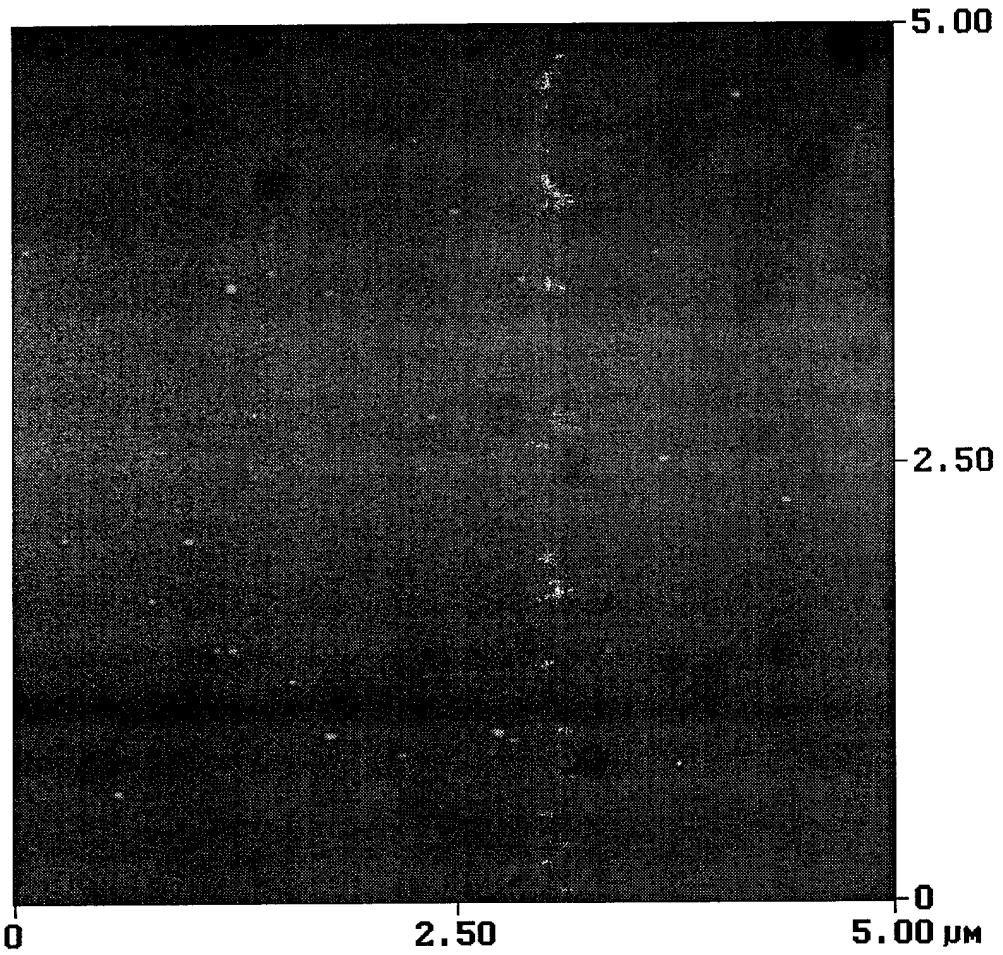


Image Statistics

Z range	11.565 nm
Mean	0.0002 nm
Rms (Rq)	0.356 nm
Mean roughness (Ra)	0.249 nm
Max height (Rmax)	11.565 nm
Surface area	25.003 µm²
Surface area diff	0.011 %

Box Statistics

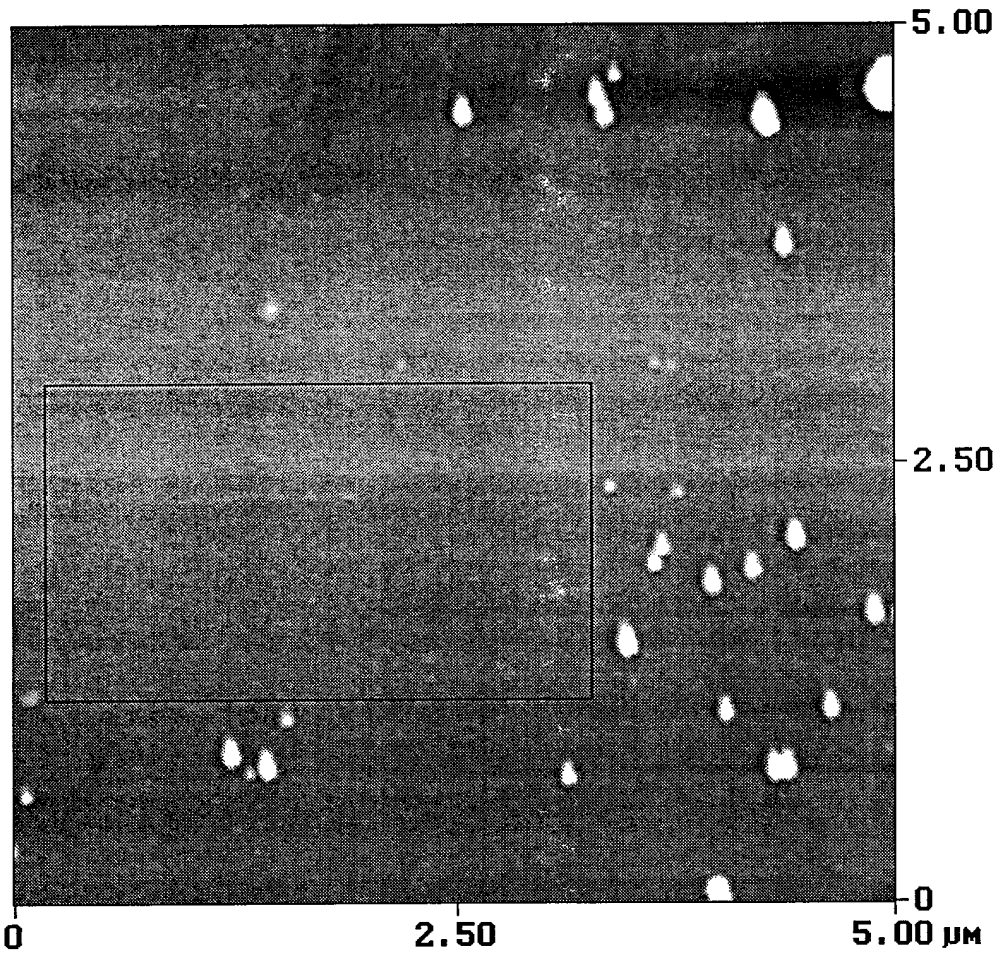
Mean
Rms (Rq)
Mean roughness (Ra)
Box x dimension
Box y dimension

Peak off | Area on | Summit off | Zero Cross off

Fig. 2

Peak Surface Area Summit Zero Crossing Stopband Execute Clear

Roughness Analysis



ZnO annealed at 500C, 0.5hr, nitrogen

Image Statistics

Z range	67.249 nm
Mean	-0.0004 nm
Rms (Rq)	2.329 nm
Mean roughness (Ra)	0.687 nm
Max height (Rmax)	67.249 nm
Surface area	25.045 µm²
Surface area diff	0.182 %

Box Statistics

Mean	0.008 nm
Rms (Rq)	0.310 nm
Mean roughness (Ra)	0.236 nm
Box x dimension	3.102 µm
Box y dimension	1.800 µm

Peak off Area on Summit off Zero Cross off

Fig. 3

Peak Surface Area Summit Zero Crossing Stopband Execute Clear

Roughness Analysis

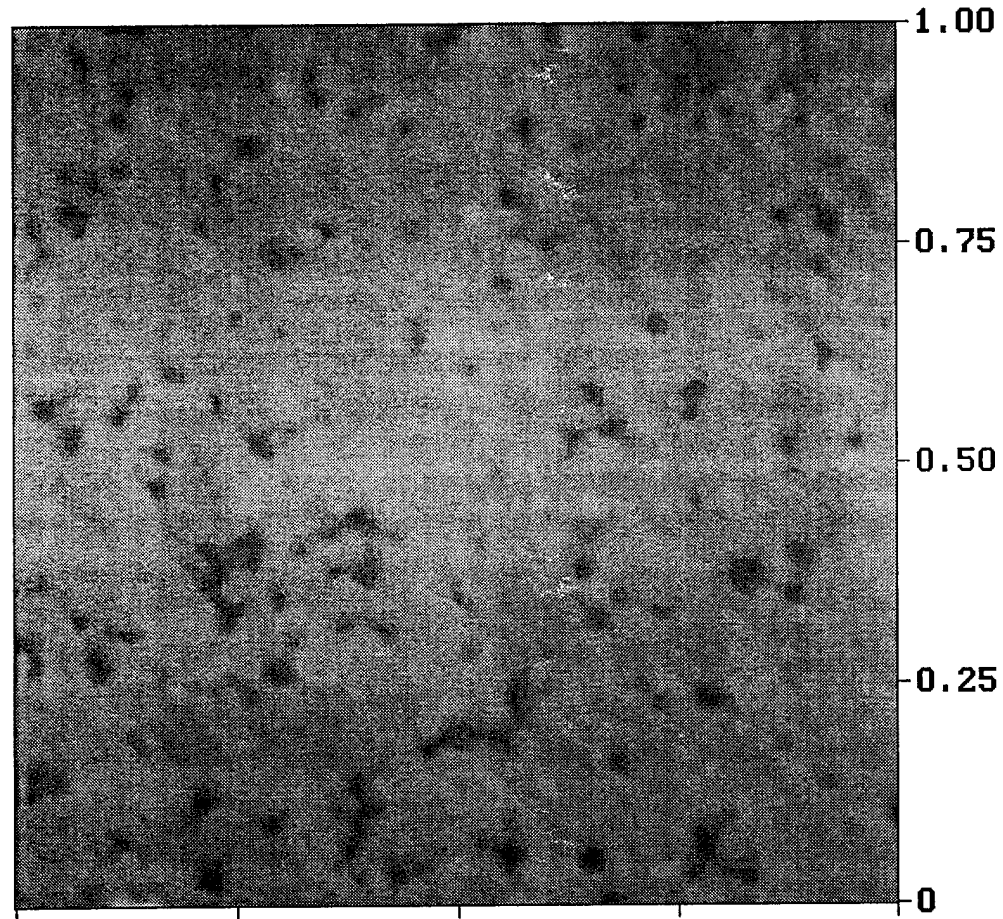


Image Statistics

Z range	3.009 nm
Mean	-0.00002 nm
Rms (Rq)	0.240 nm
Mean roughness (Ra)	0.174 nm
Max height (Rmax)	3.009 nm
Surface area	1.001 µm²
Surface area diff	0.088 %

Box Statistics

Mean
Rms (Rq)
Mean roughness (Ra)
Box x dimension
Box y dimension

Peak off Area on Summit off Zero Cross off

Fig. 4

FWHM = 165 arc-sec

Fig. 15

Omega 16.49300 Phi 90.0 X 1.5
hkl 0 0 2 2Theta 34.6250 Psi -1.100 Y 0.0

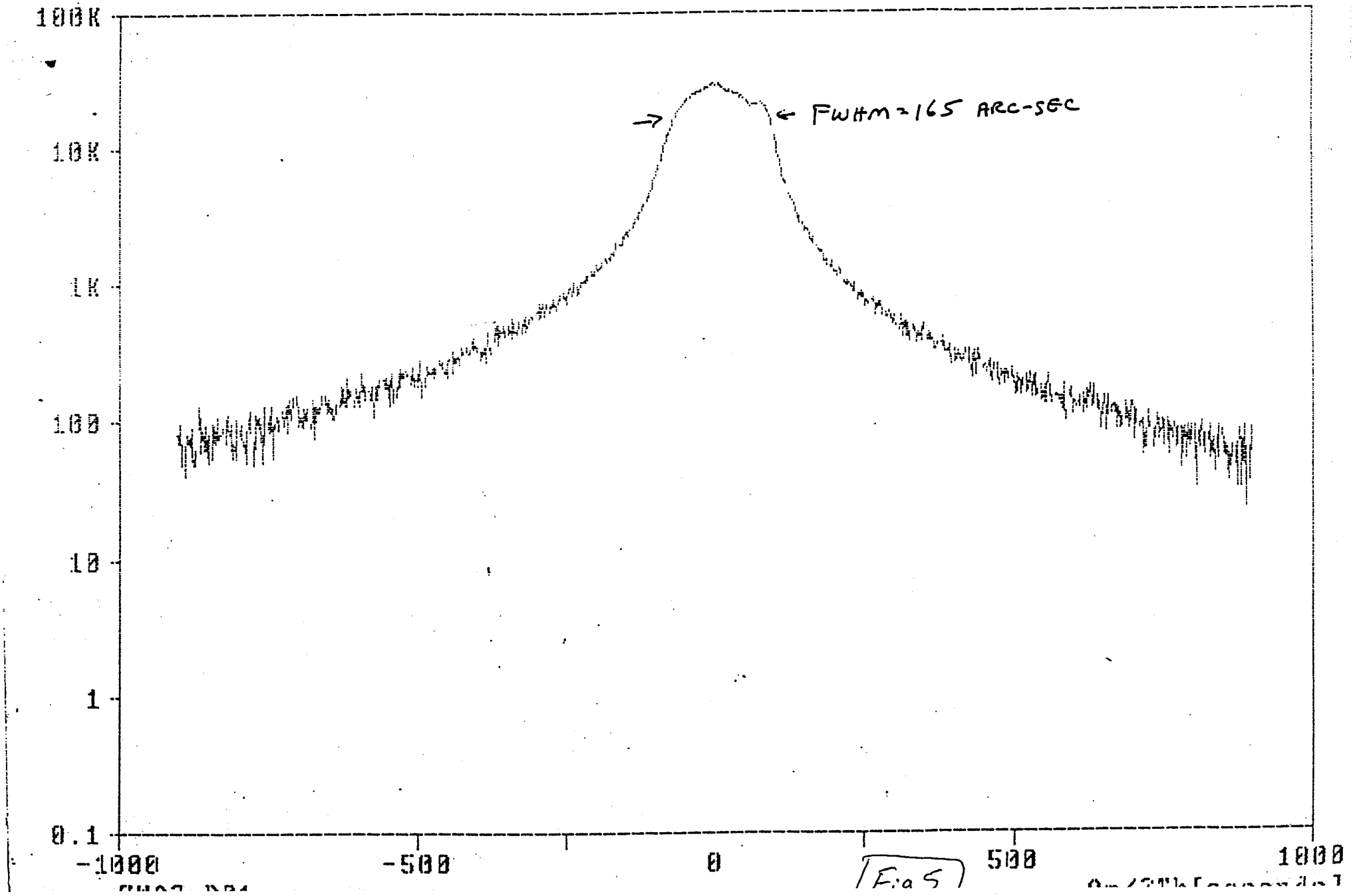


Fig 5

FIG. 17a

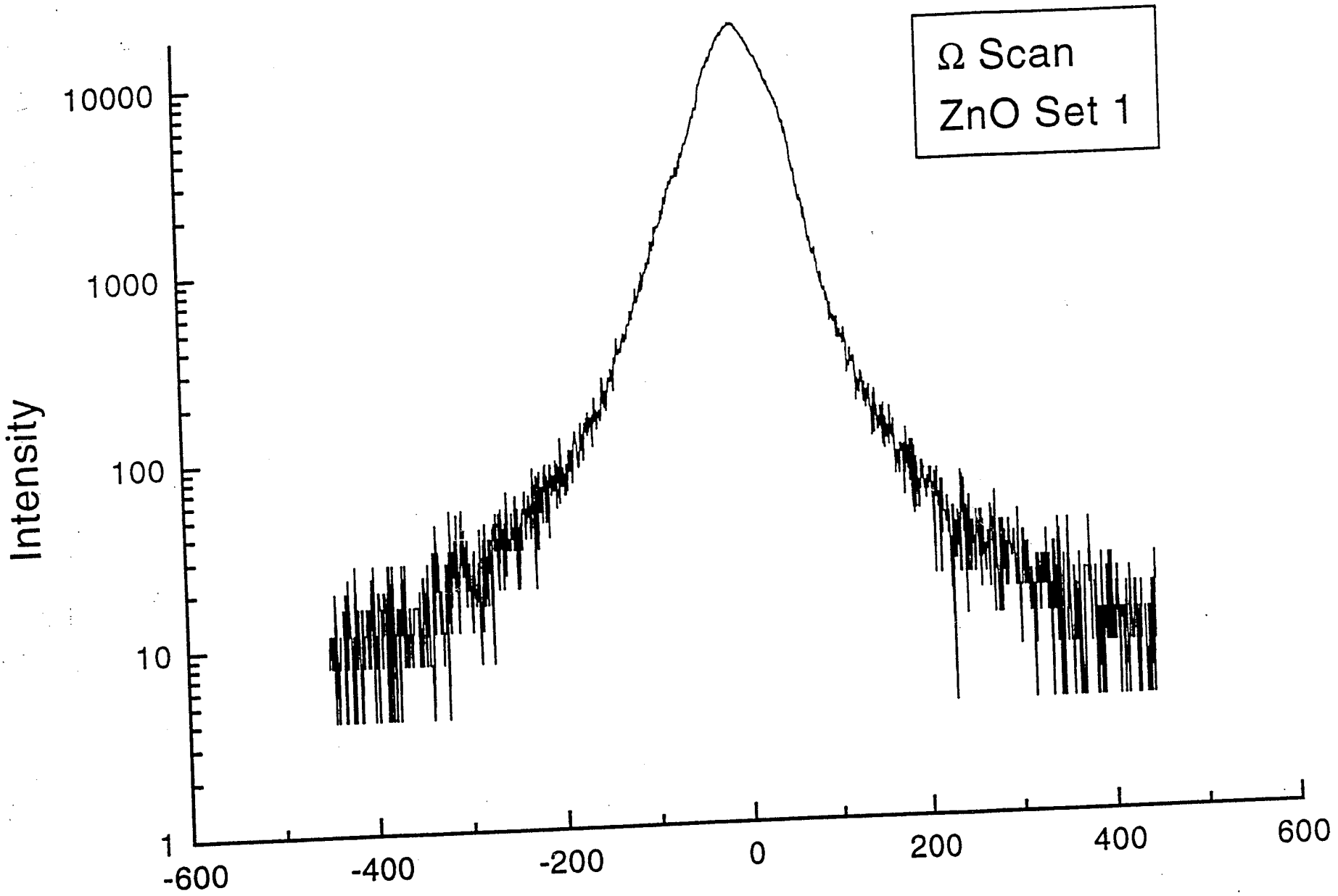

Ω Scan
ZnO Set 1
Intensity
10000
1000
100
10
1
-600
-400
-200
0
200
400
600

Fig. 6

FIG. 22

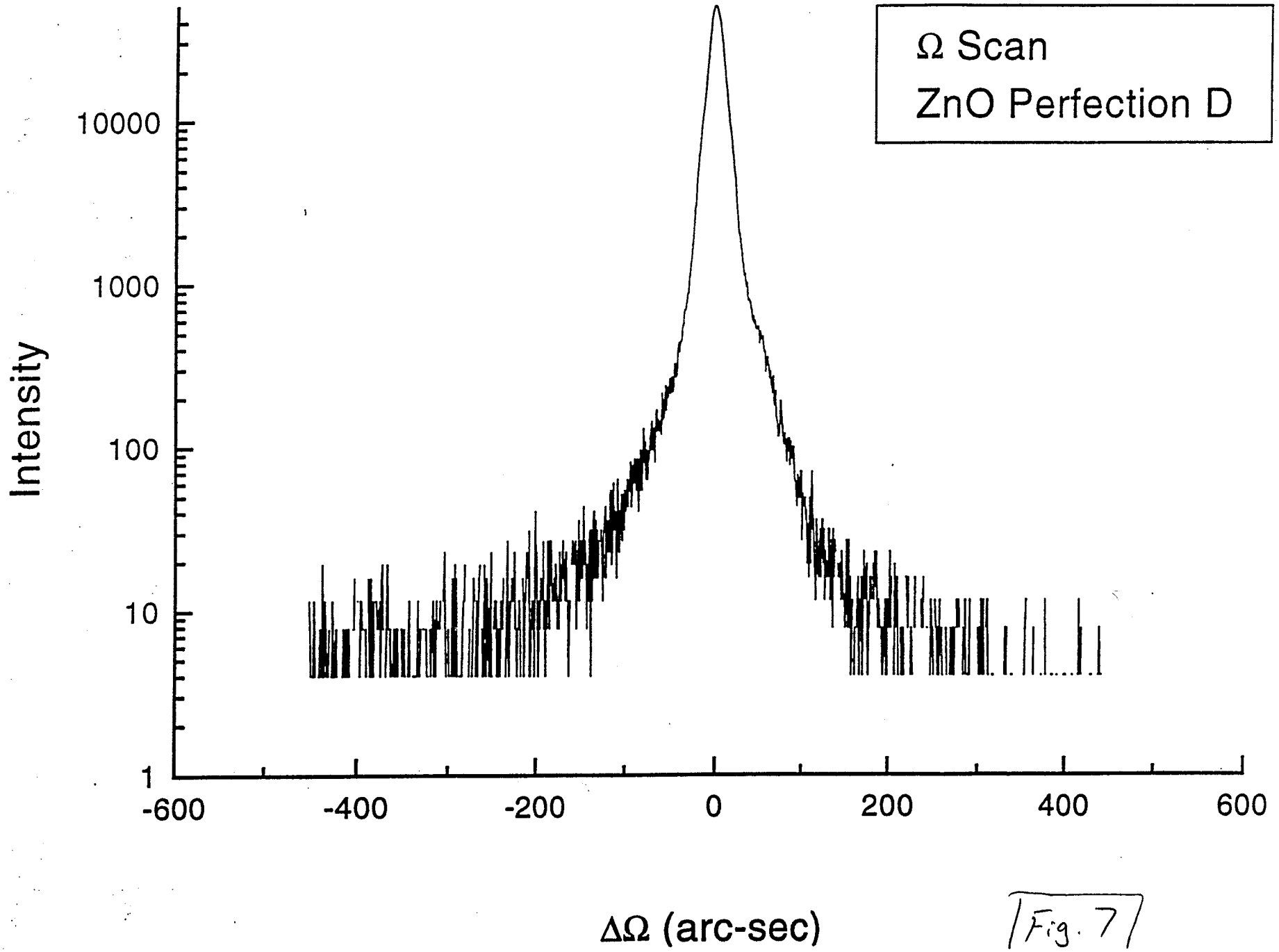

Ω Scan
ZnO Perfection D
Intensity
10000
1000
100
10
1
-600
-400
-200
0
200
400
600
ΔΩ (arc-sec)

Fig. 7

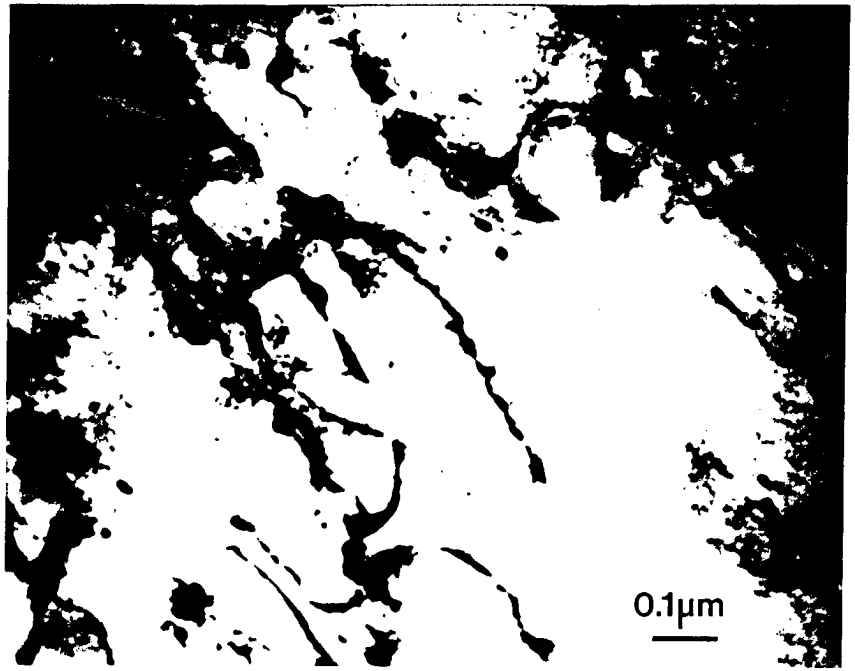
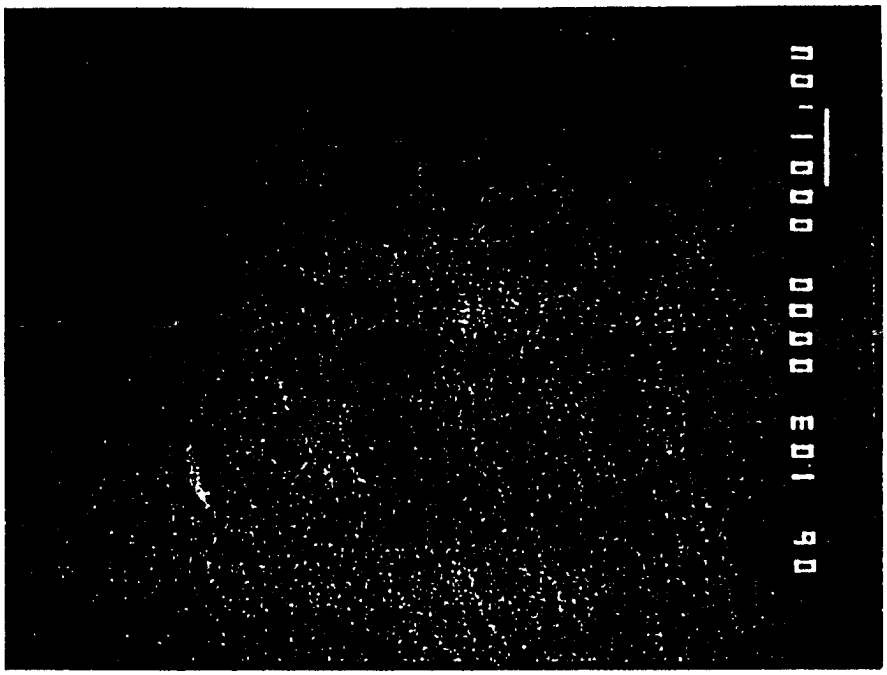


Fig. 8



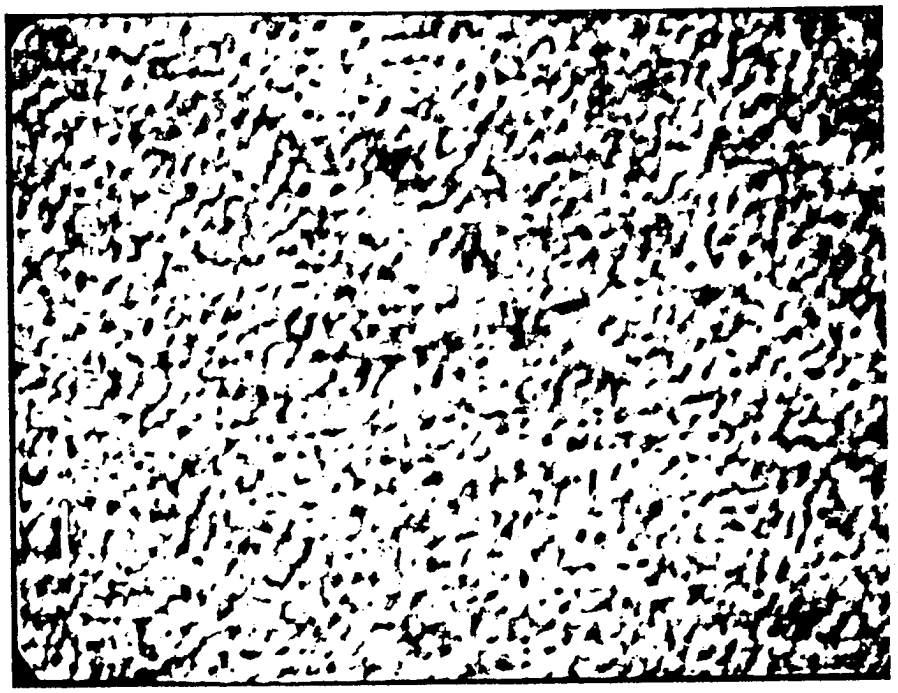


Fig. 9 — Not used